

# Sulfide-Based Solid Electrolytes for Solid-State Li Batteries

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**Oak Ridge National Laboratory**

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# Overview

## Timeline

- Project start date: Oct. 1, 2019
- Project end date: Sept. 30, 2022
- Percent complete: 30

## Budget

- FY20 Funding: \$ 500K

## Barriers

**Performance:** (i) Cell energy density, 500 Wh/Kg -1000 cycles (ii) Stable ionic conductivity  $> 10^{-4}$  S/cm at room temperature

**Interfacial Stability:** Chemical and electrochemical stability 0 – 4.5 V wrt  $\text{Li}^0/\text{Li}^+$

**Current Density** : 2 mA/cm<sup>2</sup> or higher

## Partners/Collaborators

- *Pacific Northwest National Laboratory*  
Electron Microscopy –Chongmin Wang
- Virginia Commonwealth University  
Interface Modelling – Prof. Puru Jena
- Hunter's College, New York  
NMR Studies - Prof. Steve Greenbaum

## Impact

Solid electrolytes with high Li<sup>+</sup> conductivity and stable interfaces are critical to the development of all solid-state batteries that meets EV goals in terms of energy density and life

## Objectives

- Synthesize sulfide-based superionic conductors and evaluate their chemical and interfacial stability
- Reduce the area specific resistance (ASR) between sulfide solid electrolytes (SEs) and a Li-ion cathode
- Meet the electrochemical stability and critical current density goals for all-solid-state batteries

## **Cathode-Solid Electrolyte Interfaces :**

- Utilize *ex-situ* and *in-situ* Raman, NMR, X-ray, and electron microscopy methods to characterize cathode/SE interfaces and correlate with electrochemical performance
- Develop coating strategies to improve interfacial compatibility between sulfide-based SEs and high voltage cathodes (e.g., Ni-rich NMC)

## Relevance to VTO Mission

R&D effort on solid state electrolytes and interfaces are critical to meet the VTO's long term goal of attaining cell energy density  $\geq 500$  Wh/Kg and 1000 EV cycles.

# Milestones

Due Date	Description	Status
12/31/2019 (Q1)	Identify synthesis, doping, and processing conditions to prepare $\text{Li}_3\text{PS}_4$ -based SEs with a $\text{Li}^+$ conductivity exceeding $10^{-4}$ S/cm	Complete
03/31/2020 (Q2)	Develop binder systems for $\text{Li}_3\text{PS}_4$ family of SEs for improving processability and stability at the Li-metal and cathode interfaces	Complete
06/30/2020 (Q3)	Measure and compare the $\text{Li}^+$ diffusion coefficient for pristine $\text{Li}_3\text{PS}_4$ and substituted $\text{Li}_3\text{PS}_4$ SEs using solid-state NMR	In progress
09/30/2020 (Q4)	Undertake <i>in-situ</i> Raman and electron microscopy including cryo-TEM for characterizing $\text{Li}_3\text{PS}_4$ and cathode- $\text{Li}_3\text{PS}_4$ interfaces as part of determining the ASR	In progress

# Li<sup>+</sup> conducting sulfide-based solid electrolytes (SEs) have several advantages compared to their oxide counterparts

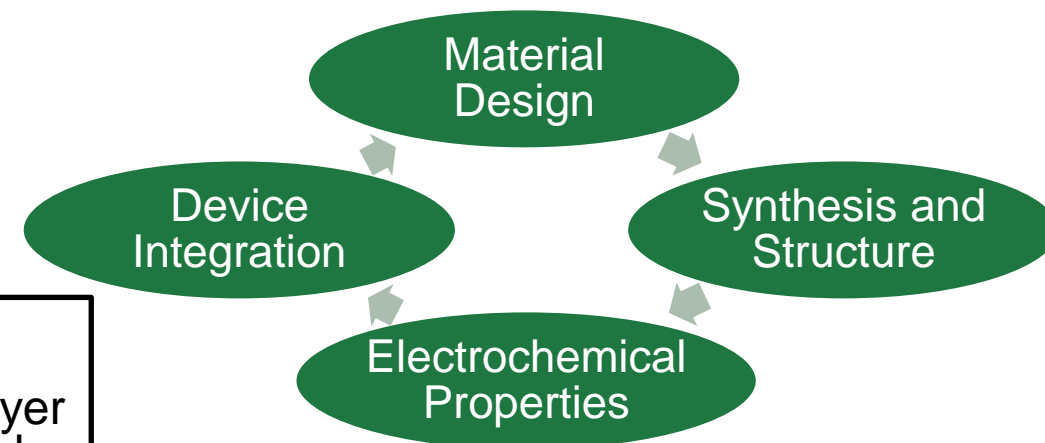
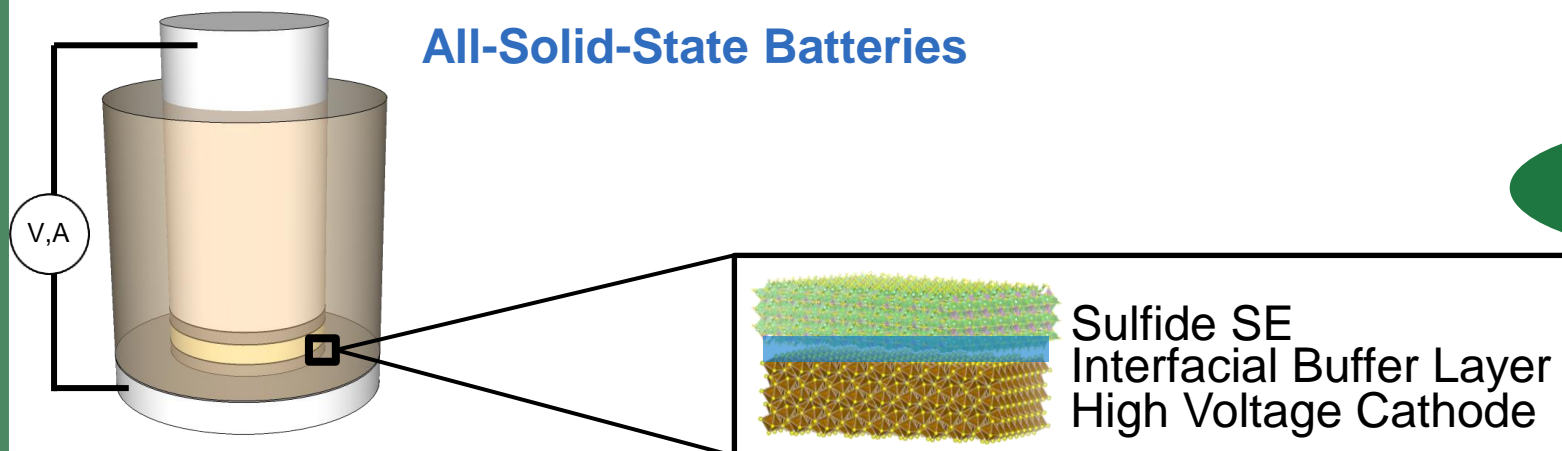
## Sulfide SE Advantages

- Superionic conductivity ( $\geq 10^{-4}$  S/cm at 25°C)
- Scalable, low temperature synthesis: solvent-mediated routes enable control over composition, structure, and crystallinity
- Soft mechanical properties enable cold-pressing
- Earth abundant and potentially low cost

## Challenges

- Chemically unstable in air
- Narrow electrochemical stability window
- Integration into solid-state batteries
  - Cathode/electrolyte interface
  - Li/electrolyte interface

## All-Solid-State Batteries

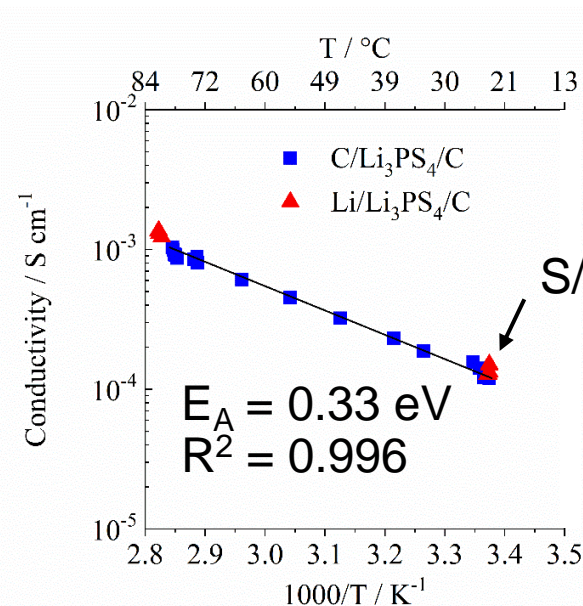
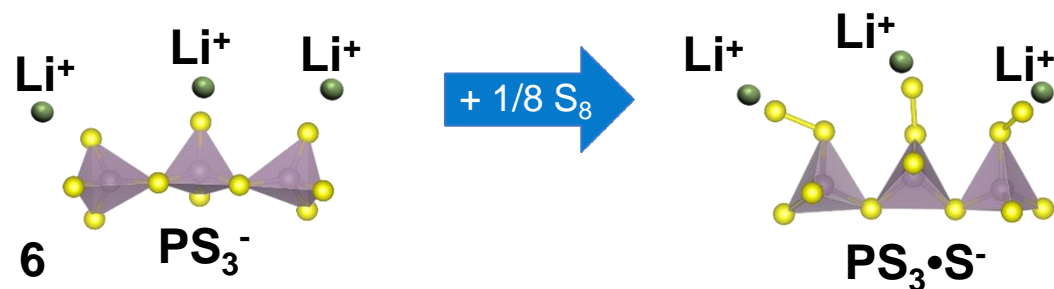
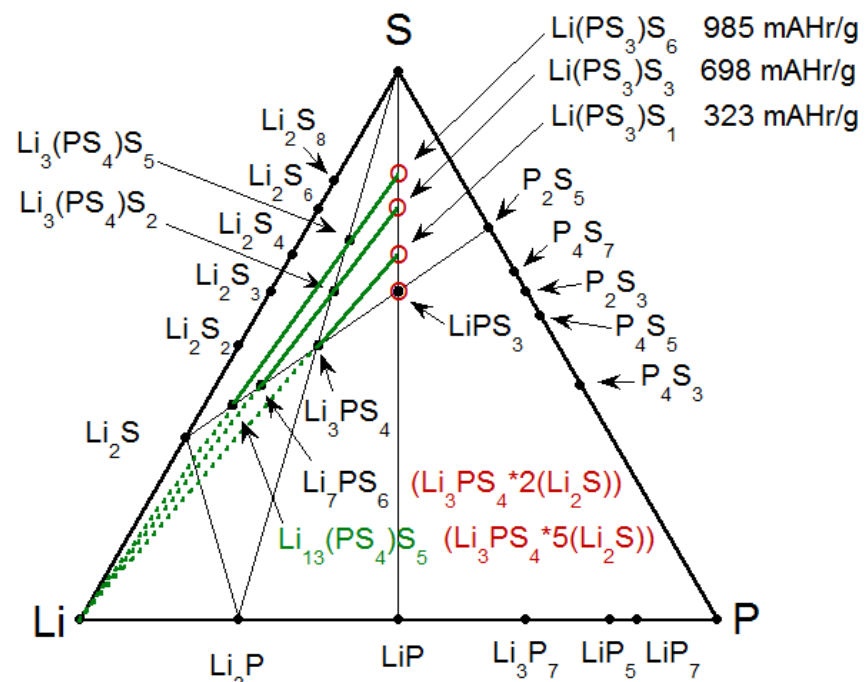


## Key Project Goals:

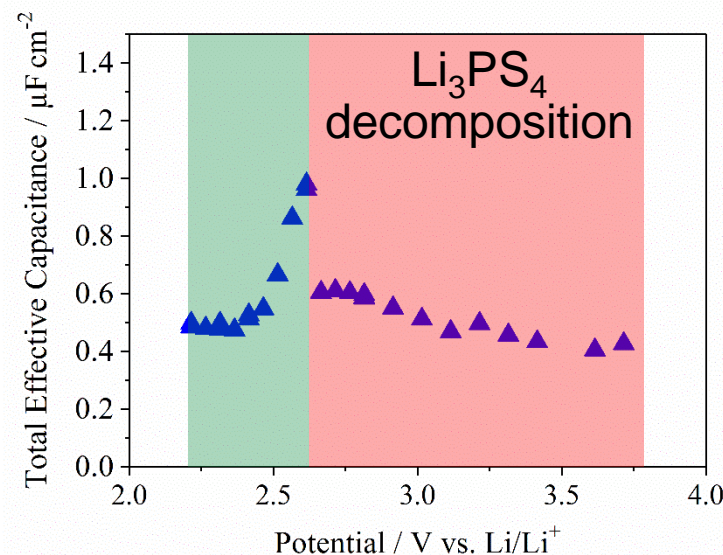
1. Synthesize superionic sulfide SEs using **scalable, solvent-mediated routes**
2. Develop **sulfide/polymer composite SEs** which can be tape cast into layers <30  $\mu\text{m}$  thick.
3. Improve cathode/sulfide SE compatibility via **interfacial buffer layers**.

Efforts in FY19 focused on solvent-mediated synthesis and characterization of  $\beta$ - $\text{Li}_3\text{PS}_4$  solid electrolyte and sulfur-catenated thiophosphate cathodes.

## High Capacity Sulfur-Catenated Cathodes Based on Phase Diagram Analysis



**Demonstrated superionic conductivity of  $\beta$ - $\text{Li}_3\text{PS}_4$  in blocking and nonblocking cells**



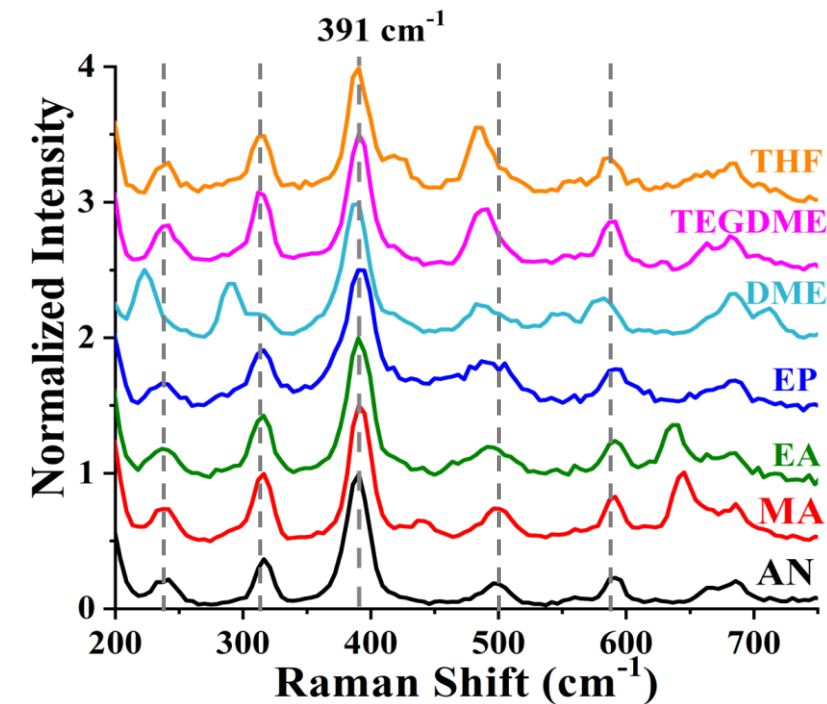
**Identified oxidative stability limit (2.6 V vs.  $\text{Li}/\text{Li}^+$ ) for  $\beta$ - $\text{Li}_3\text{PS}_4$  using EIS**

$\text{Li}_2\text{P}_2\text{S}_6$  is an important intermediate in the solvent-mediated synthesis of lithium thiophosphate superionic conductors. Understanding formation of this species is critical for optimizing synthesis route.

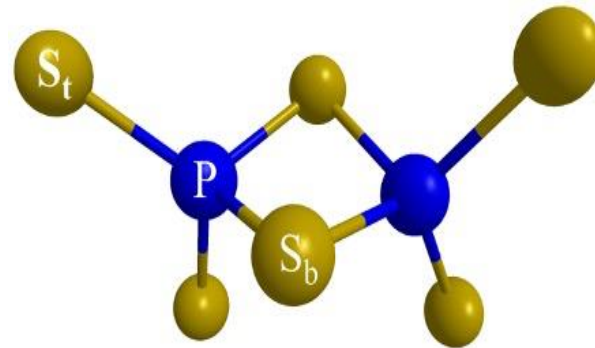
## Experimental Details

- $\text{Li}_2\text{S} + \text{P}_2\text{S}_5$  (1:1 molar ratio) **dissolved** in various solvents
- All synthesis/characterization performed under Ar

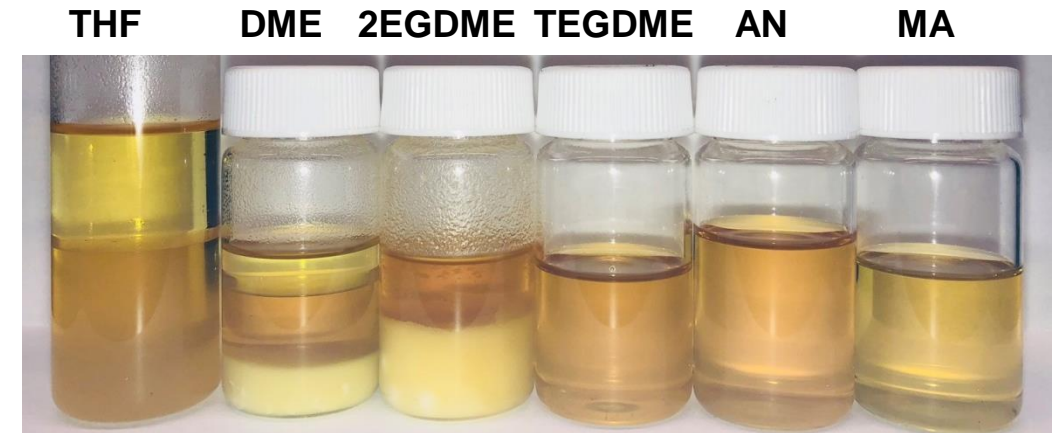
## Raman spectra of $\text{Li}_2\text{P}_2\text{S}_6$ in Various Solvents



Structure of solvated  $\text{Li}_2\text{P}_2\text{S}_6$  is virtually identical in a wide range of solvents.



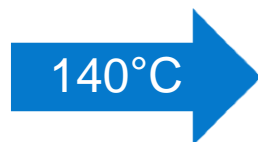
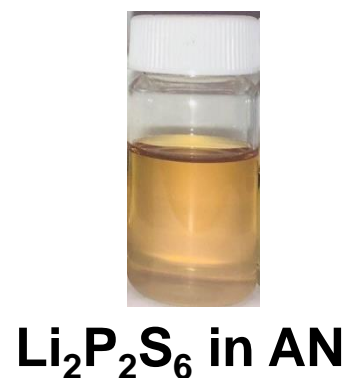
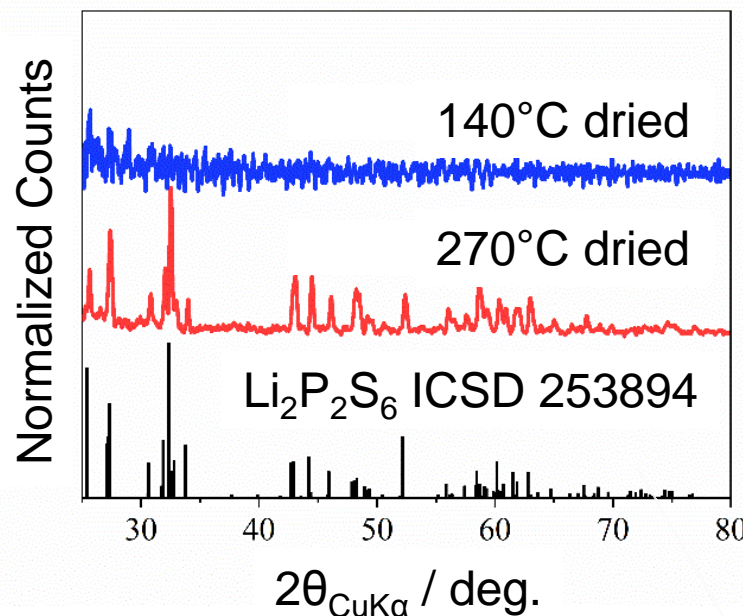
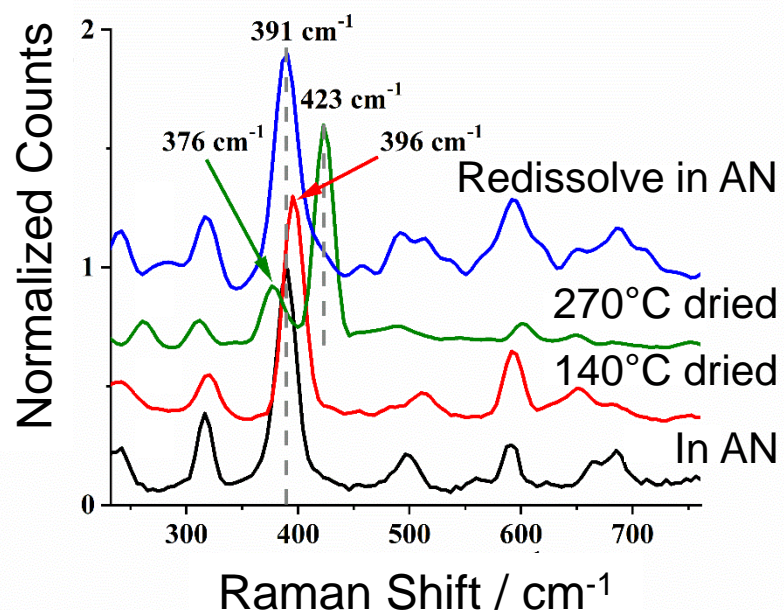
## $\text{Li}_2\text{P}_2\text{S}_6$ -based Solutions



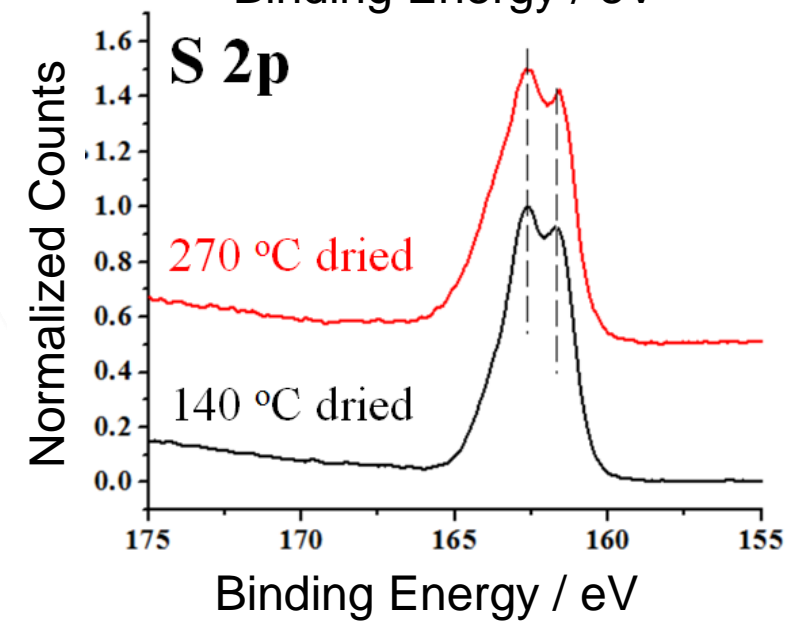
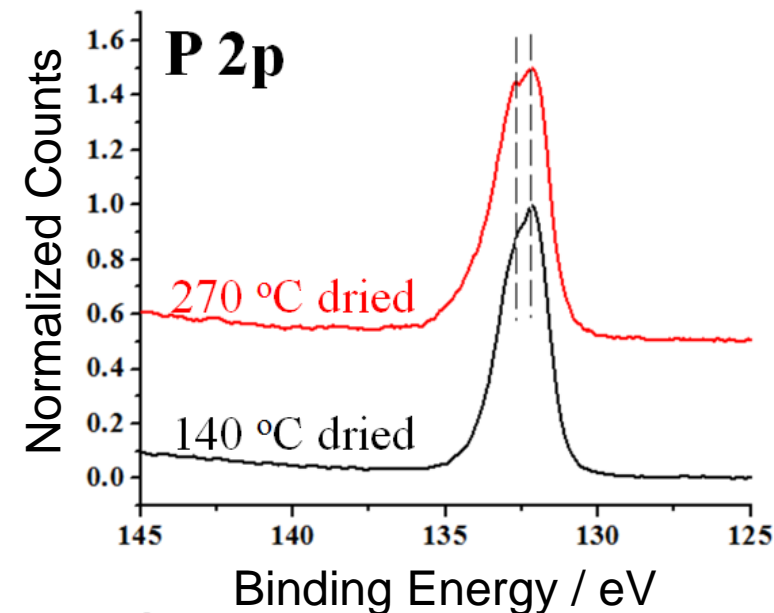
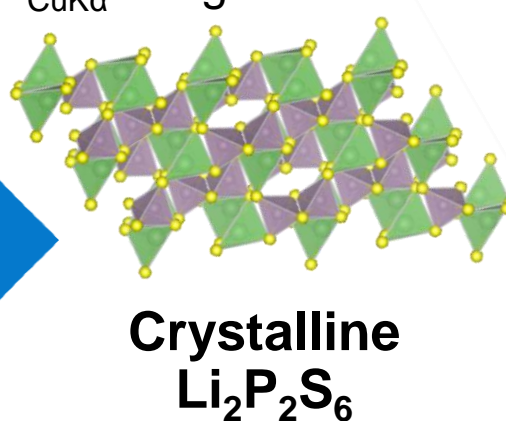
Raman Shift / $\text{cm}^{-1}$	Peak Assignment
239	$\delta(\text{S}_b\text{-P-S}_t) + \delta(\text{S}_t\text{-P-S}_t)$
315	$\nu(\text{P-P}) + \delta(\text{S}_b\text{-P-S}_t) + \nu(\text{P-S}_t)$
391	$\nu(\text{P-S}_b) + \nu(\text{P-S}_t)$
423	$\nu(\text{P-S}_b)$
500	$\nu(\text{P-S}_b)$
591	$\nu(\text{P-S}_b) + \nu(\text{P-S}_t) + \nu(\text{P-P})$
687	$\nu(\text{P-S}_t) + \delta(\text{S}_t\text{-P-S}_t)$

By tuning synthesis conditions, a range of lithium thiophosphate products can be prepared, including solvated complexes, glassy, and/or crystalline materials.

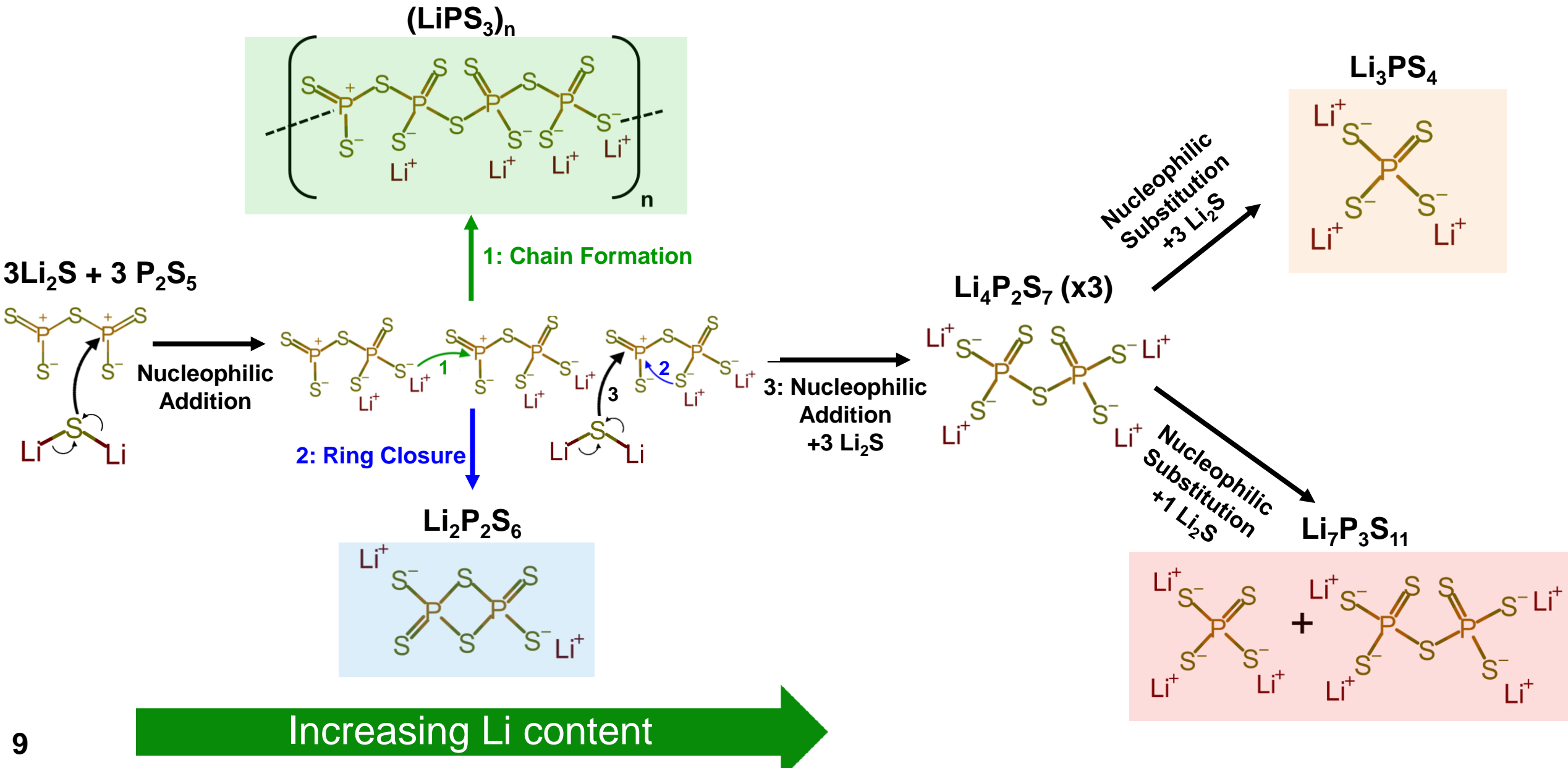
## Structural Characterization of Solvated vs. Dried $\text{Li}_2\text{P}_2\text{S}_6$



Amorphous  
 $\text{Li}_2\text{P}_2\text{S}_6$



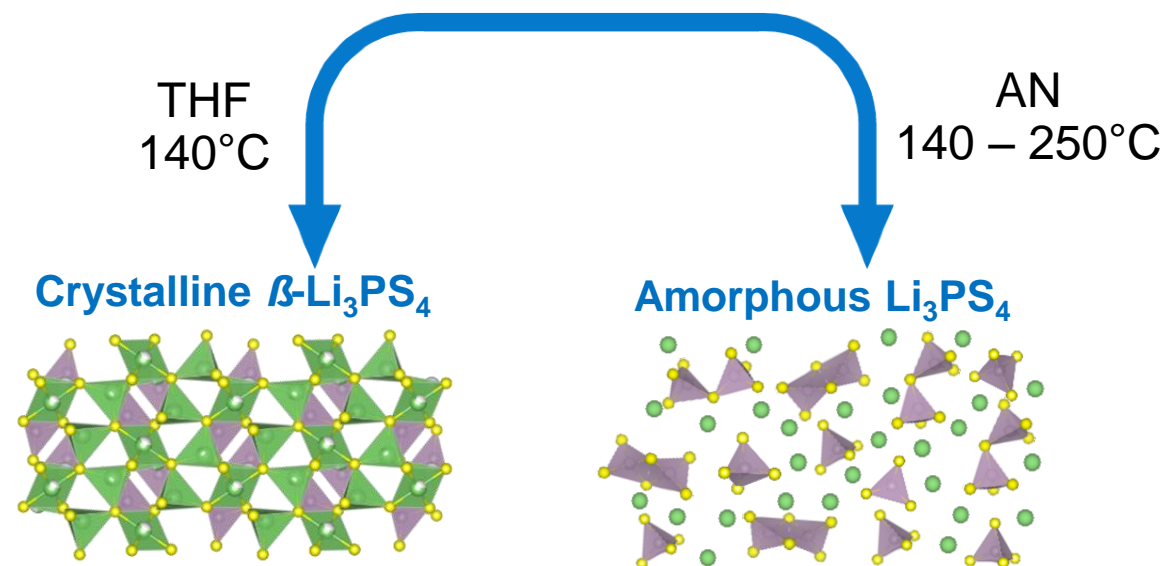
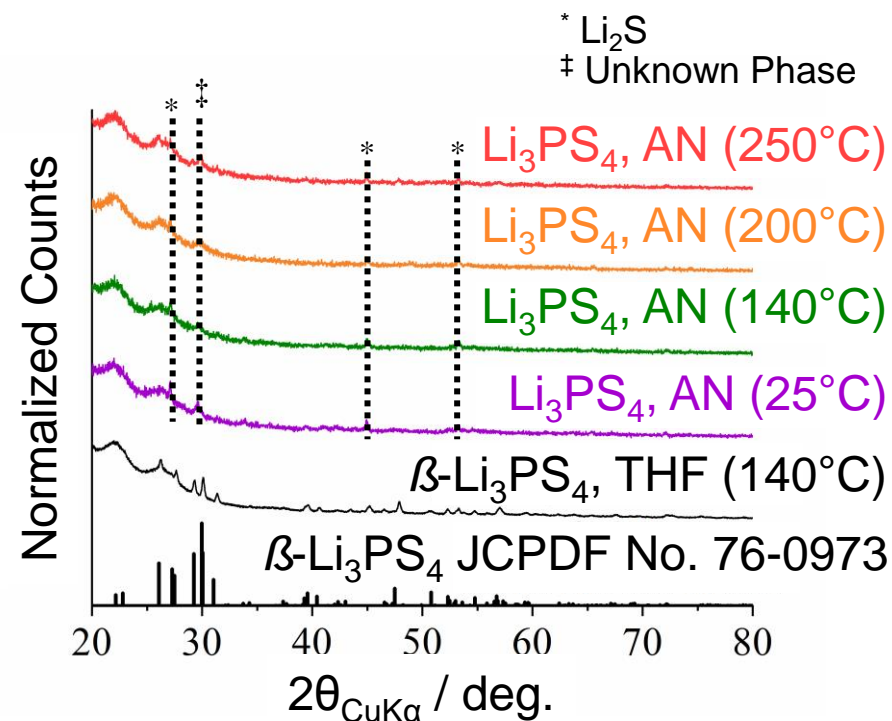
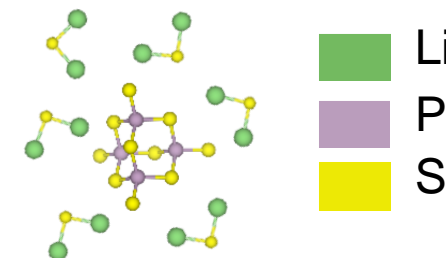
A general reaction mechanism for the solvent-mediated synthesis of lithium thiophosphates is proposed. For a given solvent, the distribution of products depends on relative reaction rates and stability of intermediates.



The structure of  $\text{Li}_3\text{PS}_4$  prepared through solvent-mediated synthesis routes is highly sensitive to the solvent and thermal treatment. Both crystalline and amorphous materials can be prepared.

### Synthesis Details

- Blend  $\text{Li}_2\text{S}$  +  $\text{P}_2\text{S}_5$  (3/1 molar ratio) in solvent (THF or AN)
- Dry at 25-45°C under vacuum
- Anneal at 140-250°C under Ar



Note: amorphous  $\text{Li}_3\text{PS}_4$ -like product contains several polyanionic groups including  $\text{PS}_4^{3-}$ ,  $\text{P}_2\text{S}_6^{2-}$ , and  $\text{P}_2\text{S}_7^{4-}$ .

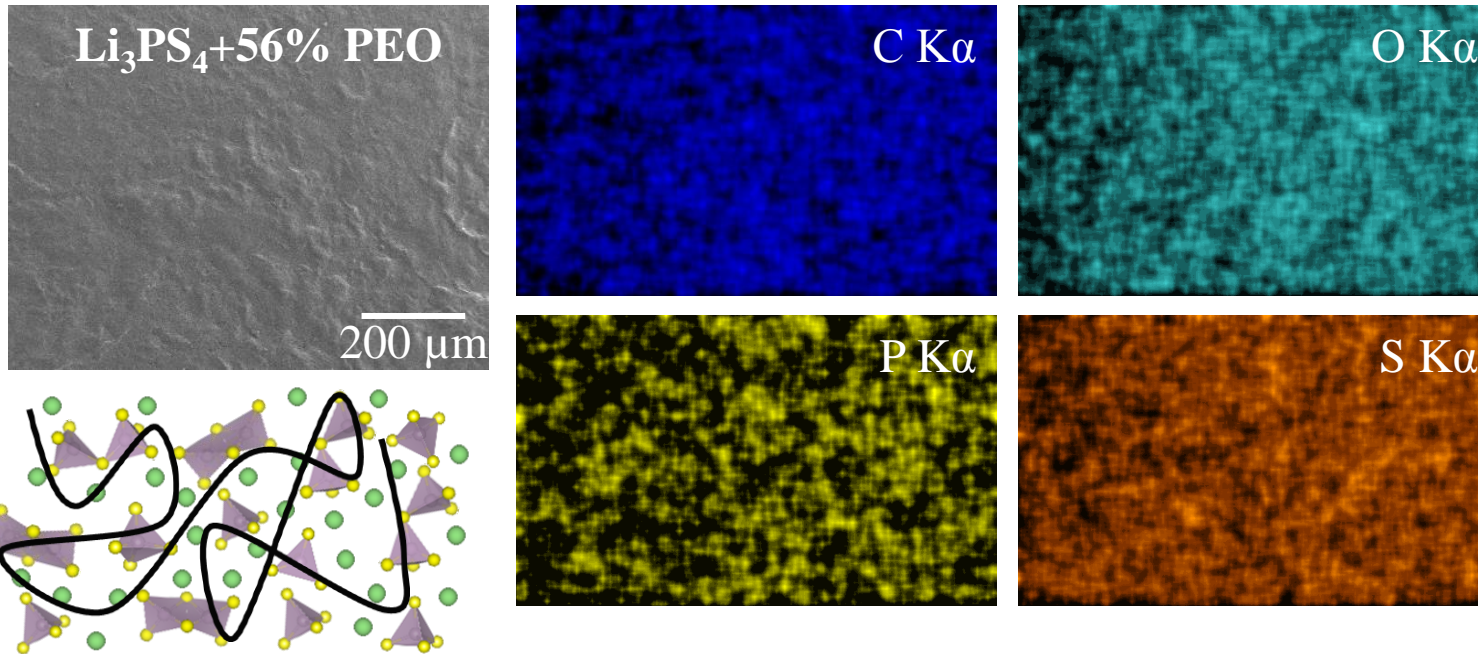
1. In THF, crystalline  $\beta\text{-Li}_3\text{PS}_4$  forms after annealing at 140°C, but acetonitrile solvent results in amorphous product.
2. Compared to polycrystalline  $\beta\text{-Li}_3\text{PS}_4$ , amorphous  $\text{Li}_3\text{PS}_4$  may promote more uniform Li plating/stripping in SSBs.

A new class of composite SEs containing amorphous  $\text{Li}_3\text{PS}_4$  synthesized *in-situ* in the presence of a PEO binder was developed. Structure, conductivity, and processability of these materials were studied extensively in FY20.

Technical Accomplishment

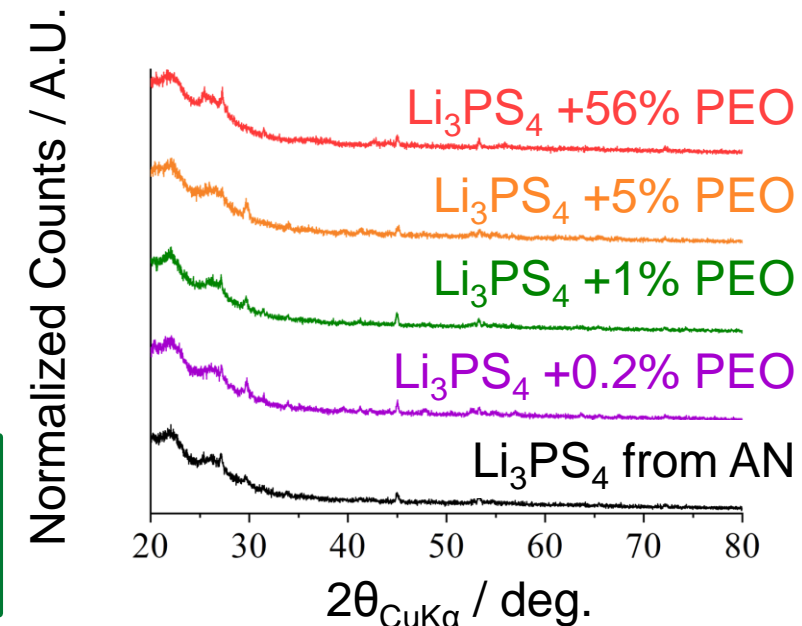
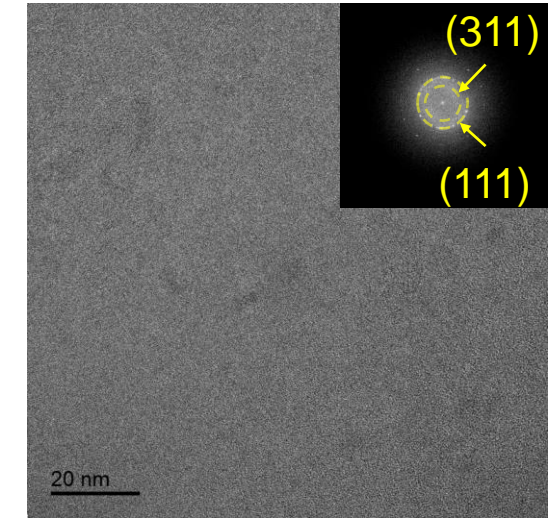
### Experimental Details

- Blend  $\text{Li}_2\text{S}$  +  $\text{P}_2\text{S}_5$  + PEO (600 kDa, 0.2 – 56 wt%) in acetonitrile
- Dry at 25-45°C under vacuum
- Anneal at 140-250°C → synthesize  $\text{Li}_3\text{PS}_4$  *in-situ*
- All work performed under argon



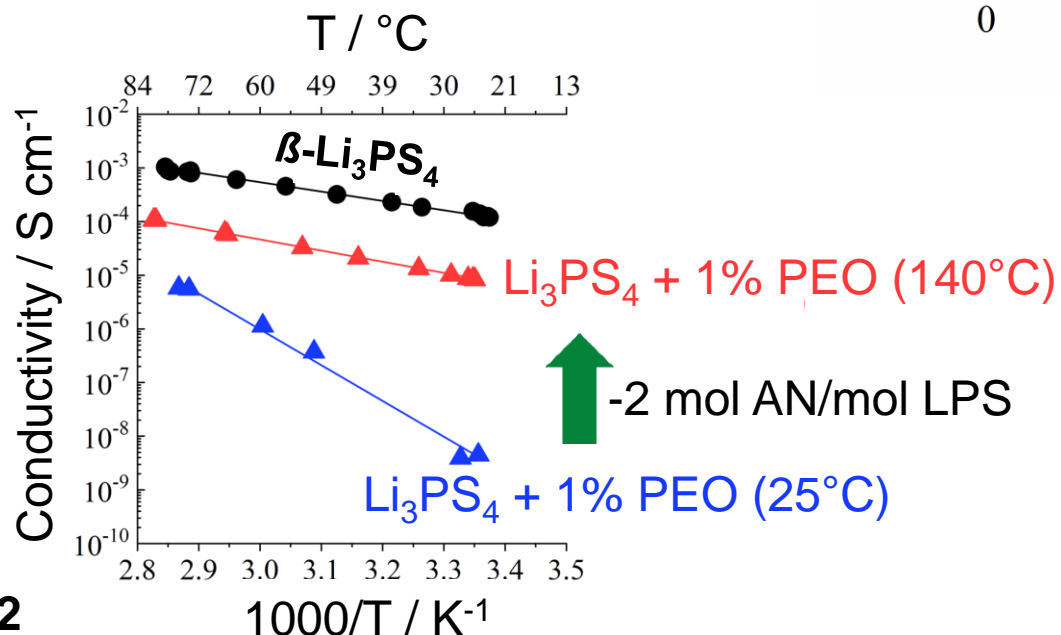
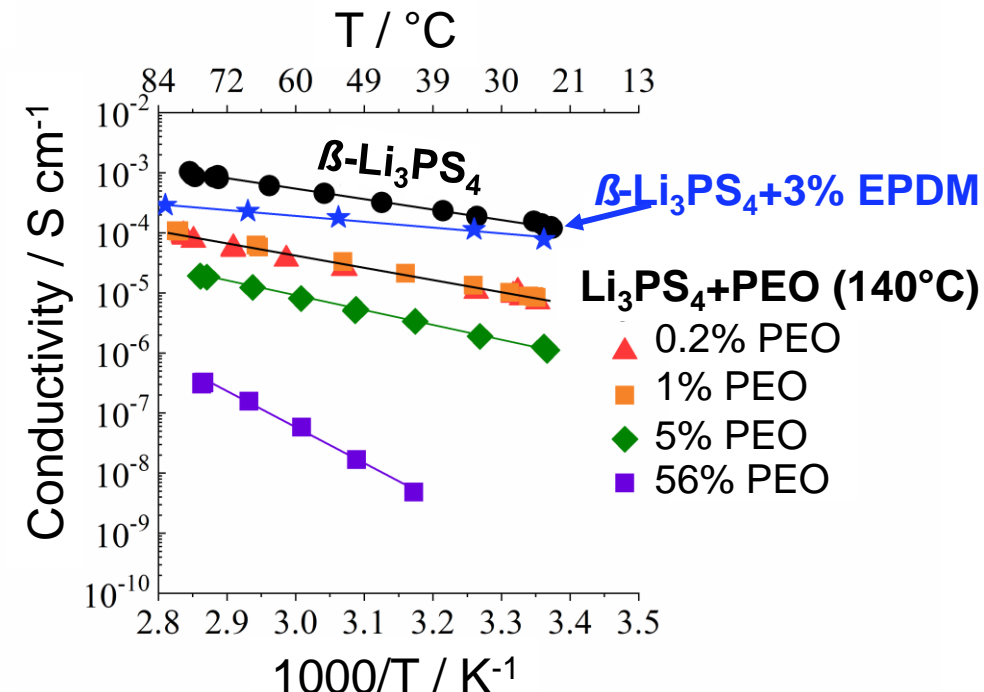
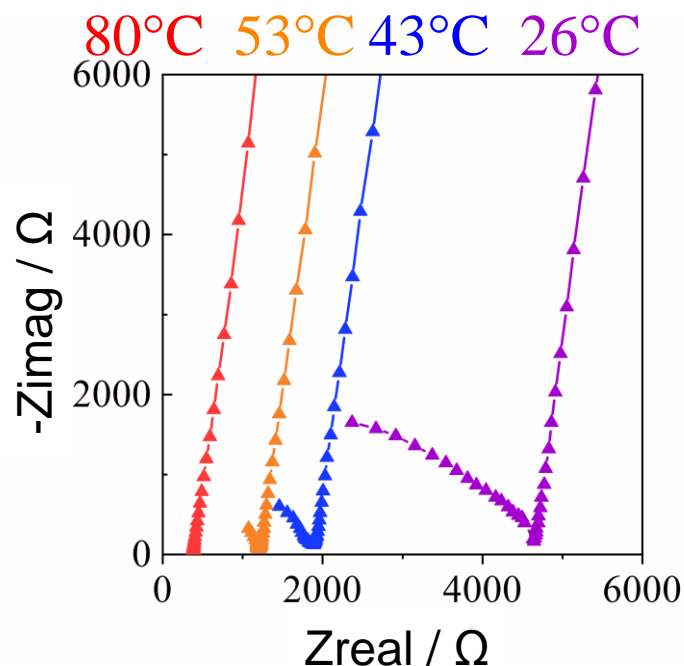
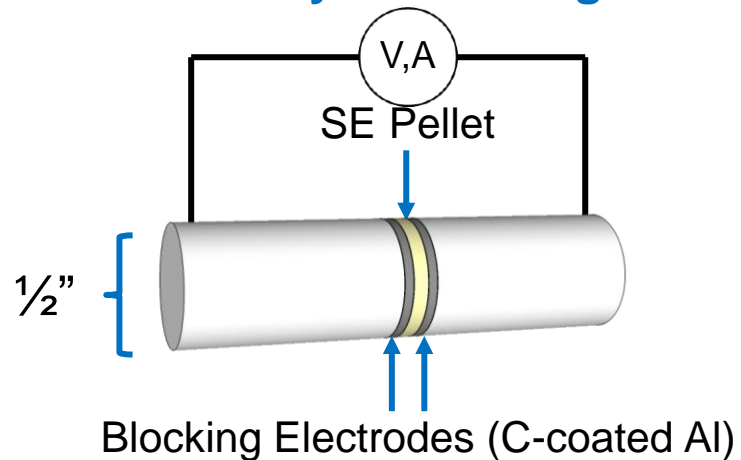
1. *In-situ* synthesis approach yields intimate blend of  $\text{Li}_3\text{PS}_4$  and binder.
2.  $\text{Li}_3\text{PS}_4$  is almost entirely amorphous except for trace amounts of crystalline  $\text{Li}_2\text{S}$  which indicates material is slightly Li deficient ( $\text{Li}_{3-x}\text{PS}_4$ )

### Cryo-TEM of $\text{Li}_3\text{PS}_4$ +1% PEO



$\text{Li}^+$  conductivity of  $\text{Li}_3\text{PS}_4/\text{PEO}$  composites is highly dependent on the thermal treatment and polymer binder content. Moderate conductivities up to  $1 \times 10^{-4} \text{ S/cm}$  ( $80^\circ\text{C}$ ) were demonstrated.

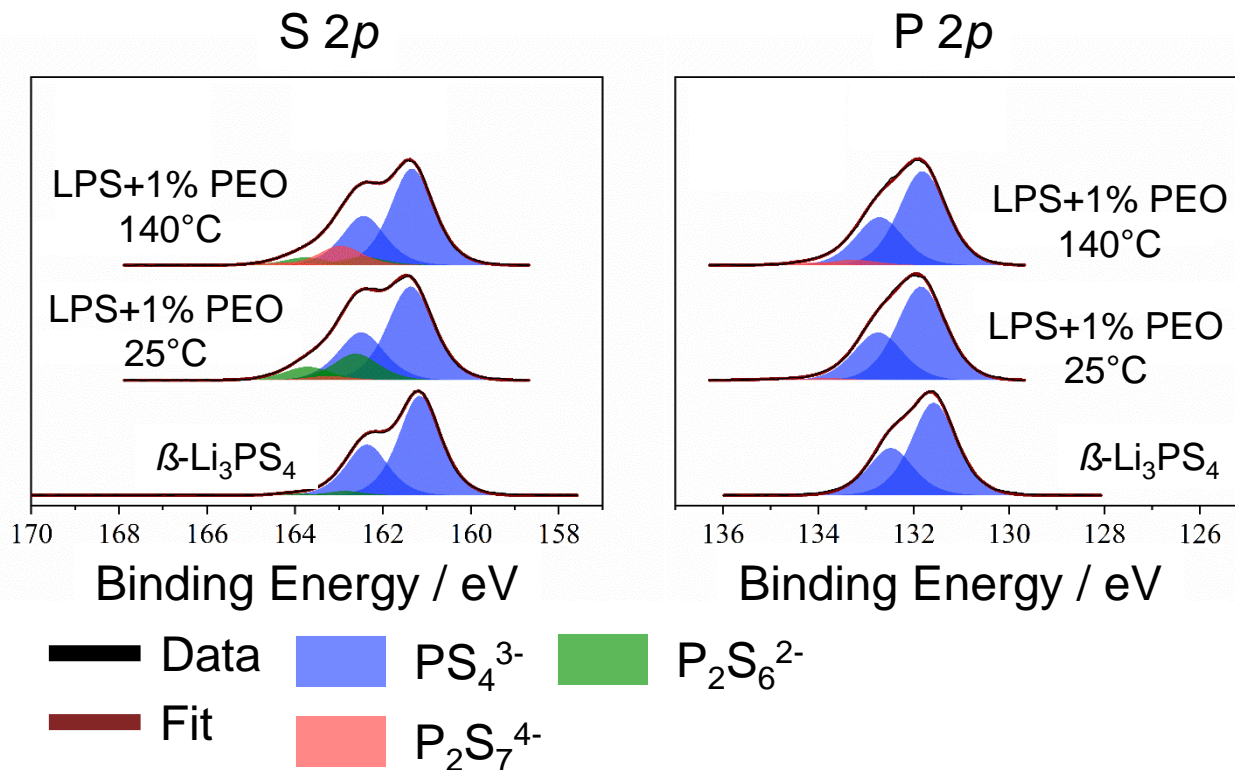
### Conductivity Cell Configuration



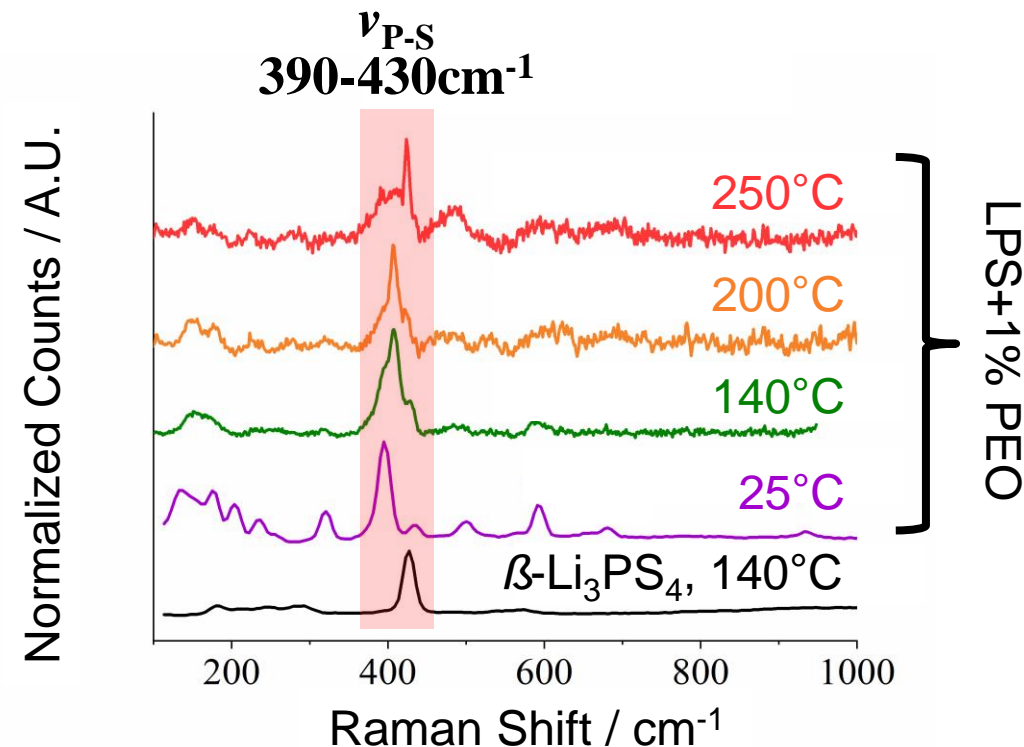
1. Coordinated acetonitrile hinders  $\text{Li}^+$  mobility and provides a less favorable energy landscape for long-range  $\text{Li}^+$  migration.
2. Polymer content should be limited to ca. 1 – 5 wt.% to ensure reasonable  $\text{Li}^+$  conductivity while providing enough binder to facilitate processing.
3. Lower conductivity of  $\text{Li}_3\text{PS}_4/\text{PEO}$  composites is due to amorphous nature of SE. Addition of 3 wt% EPDM binder to  $\beta\text{-Li}_3\text{PS}_4$  had only a minor impact on  $\text{Li}^+$  conductivity.

Effects of annealing temperature on microstructure of amorphous  $\text{Li}_3\text{PS}_4$  was studied using various spectroscopic techniques. High temperature treatment promotes formation of  $\text{P}_2\text{S}_7^{4-}$  and  $\text{PS}_4^{3-}$  moieties which increase  $\text{Li}^+$  mobility.

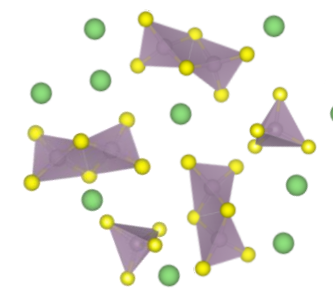
Normalized Counts / A.U.



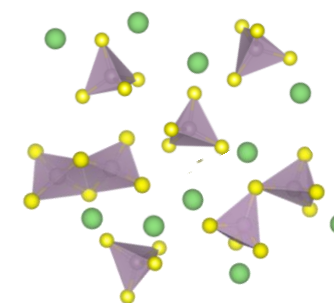
1. Amorphous  $\text{Li}_3\text{PS}_4$  dried at 25°C contained significant amount of  $\text{P}_2\text{S}_6^{2-}$  polyanions which resulted in poor  $\text{Li}^+$  conductivity.
2.  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  content increases at  $T \geq 140^\circ\text{C}$
3. Thermal decomposition occurs  $\sim 250^\circ\text{C}$



Dried at 25°C



Annealed at 140 °C



$\sigma_{\text{Li}^+, 25^\circ\text{C}}$ :  $4.5 \times 10^{-9} \text{ S/cm}$

$8.4 \times 10^{-6} \text{ S/cm}$

Slurry cast amorphous  $\text{Li}_3\text{PS}_4/\text{PEO}$  layers ( $<50\mu\text{m}$ ) were fabricated, and optimization of SE and slurry composition is in progress

### Experimental Details

- Amorphous  $\text{Li}_3\text{PS}_4$  + 5% PEO dispersed in acetonitrile
- 18 wt% solids in slurry
- Cast onto  $15\mu\text{m}$  Cu foil inside Ar glovebox
- Dried film at room temperature under vacuum overnight

**Target:** Thin, flexible SE films for SSBs



Substrate should be either:

- (i) Removable (freestanding LPS/PEO film)
- (ii) Electrode layer for SSB assembly

**As-Cast SE**



**Compacted SE Layer**

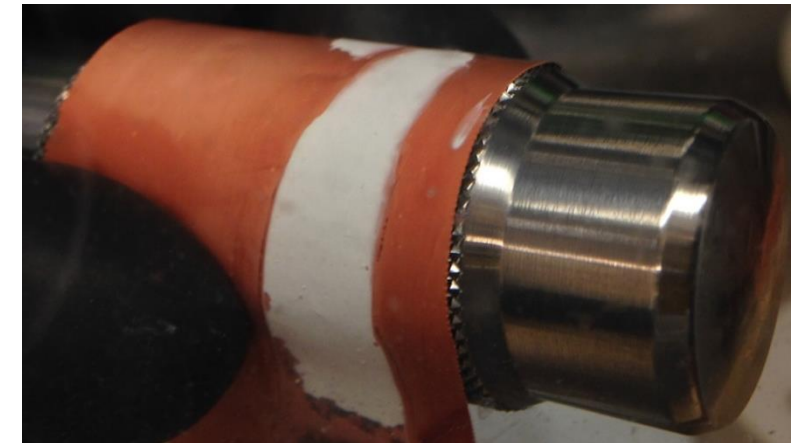


530 MPa

Cracks/flaking cause short-circuit during conductivity measurements. More optimization required.

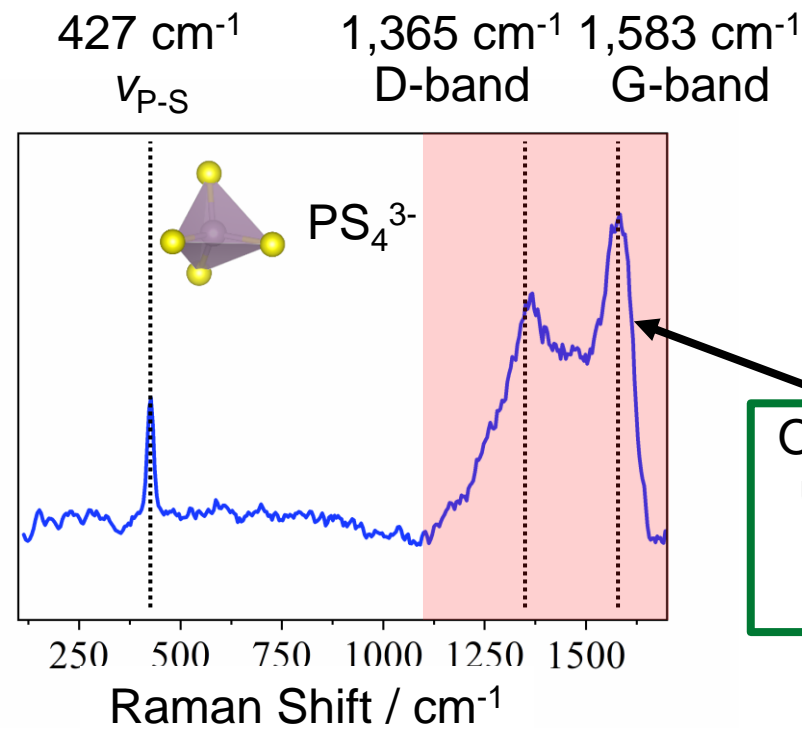
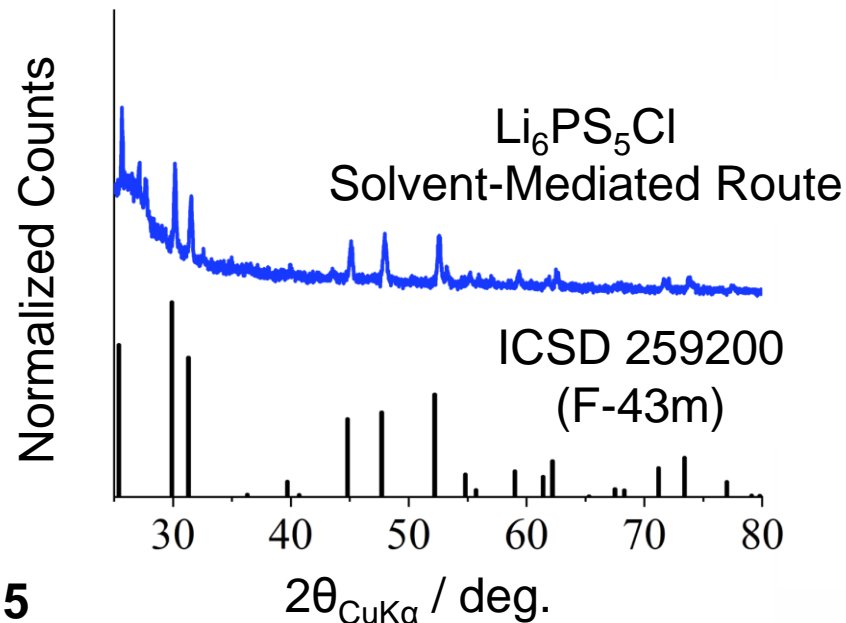
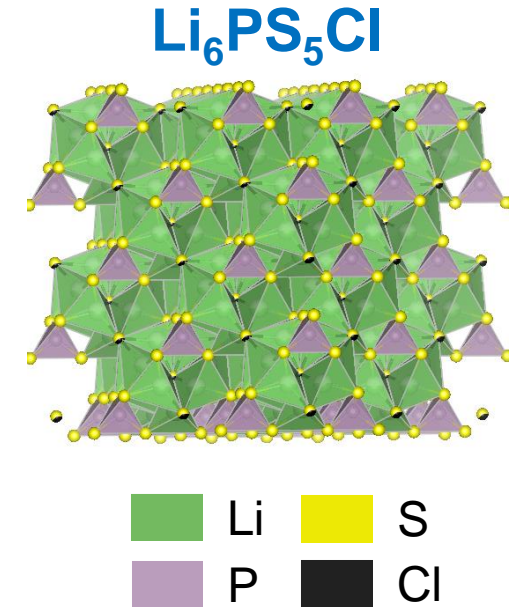
$\text{Li}_3\text{PS}_4$ +5% PEO	Thickness ( $\mu\text{m}$ )	Loading ( $\text{mg}/\text{cm}^2$ )	Density ( $\text{g}/\text{cm}^3$ )	Porosity* (%)
As-Cast	32	1.82	0.57	70
Compacted	10	1.82	1.82	3

**$\text{Li}_3\text{PS}_4$  + 5% PEO Cast on Cu Foil**



A model argyrodite solid electrolyte ( $\text{Li}_6\text{PS}_5\text{Cl}$ ) was also synthesized using a solvent-mediated route. The material had the desired cubic structure along with an amorphous carbon phase. Optimization of the synthesis parameters (e.g., solvent selection, thermal treatment, etc.) are ongoing.

Argyrodite Compound	Synthesis Status
$\text{Li}_6\text{PS}_5\text{Cl}$	Optimizing Conditions
$\text{Li}_6\text{PS}_5\text{Br}$	Ongoing
$\text{Li}_6\text{PS}_5\text{I}$	Planned for FY21
$\text{Li}_6\text{PS}_5\text{X}_{0.5}\text{Y}_{0.5}$ (X,Y = Cl, Br, I)	Planned for FY21



Origin of carbon D/G bands is not fully understood. Carbon product may be from side reaction with coordinated solvent during annealing.



## Response to Reviewers Comments

This project was not reviewed in FY19.

# Collaborations and Coordination with Other Institutions



DFT Modeling of Interfaces  
Prof. Puru Jena



Electron Microscopy  
Dr. Chongmin Wang



Nuclear Magnetic Resonance (NMR) Studies  
Prof. Steve Greenbaum

# Remaining Barriers and Challenges

1. Integrate high voltage cathodes (e.g., Ni-rich NMC) into all-solid-state containing a sulfide SE and Li metal anode. Explore how cell chemistry and configuration (e.g., stack pressure, SE thickness, and Li excess) impact performance.
2. Quantify distribution of products obtained from solvent-mediated synthesis of sulfide SEs. Determine how final material's structure and properties are influenced by key synthesis parameters including: (i) precursors, (ii) solvent, and (iii) thermal treatment.
3. Probe the various chemical and electrochemical reactions which occur at the cathode/electrolyte interface during open-circuit storage and charge/discharge cycling. Utilize *in-situ* and *ex-situ* spectroscopy methods to study interphase reaction layers.
4. Address the issue of chemo-mechanical stability between SE and cathode. Determine fundamental materials parameters/properties to improve wettability between SE-cathode/Li interfaces

*Any proposed future work is subject to change based on funding levels*

## Proposed Future Research

1. Optimize slurry casting procedure to produce sulfide SE layers  $\leq 30\text{ }\mu\text{m}$  thick. Integrate thin SE layers into SSBs containing planar cathodes or composite porous cathodes and test SSB cells
2. Establish structure/function correlations for sulfide SEs. Explore how amorphous vs. polycrystalline SEs affect important cell properties (e.g., critical current density, Li dendrite propagation, and interfacial resistance). Combine electrochemical measurements with various structural characterization tools (e.g., solid-state NMR and neutron scattering).
3. Develop cathode interfacial coatings to improve performance of SSBs with sulfide-based SEs. Coating techniques to be explored include: (i) solution-based methods (e.g., sol-gel), (ii) RF sputtering, and (iii) atomic layer deposition (ALD).
4. Develop operando methods to for monitoring chemo-mechanical stability of solid-electrolyte cathode interfaces

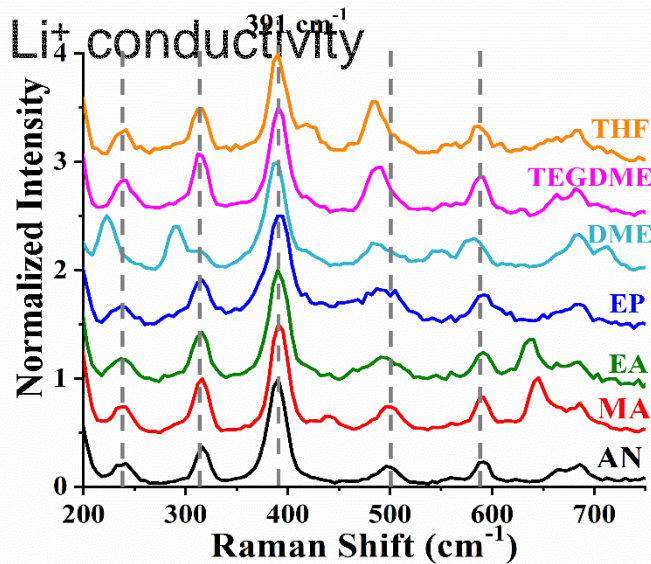
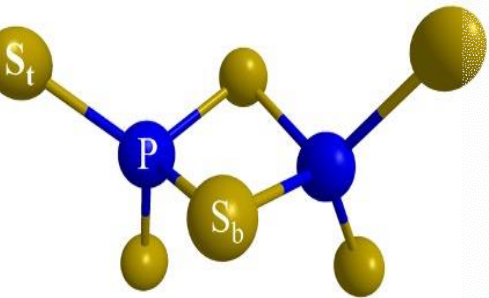
## Technical Approach:

Develop solvent-mediated synthesis routes for sulfide-based SEs

- Incorporate polymer binders through *in-situ* and *ex-situ* approaches to improve SE processability
- Utilize various characterization methods (e.g., Raman, XRD, and XPS) to understand how synthesis parameters affect structure and  $\text{Li}^+$  conductivity

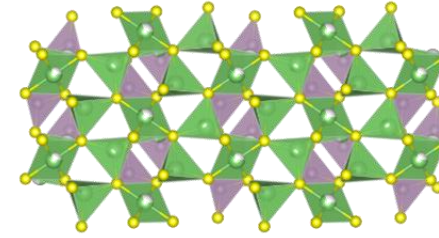
## Accomplishments:

- Proposed general reaction mechanism for lithium thiophosphate compounds prepared through solvent-mediated synthesis routes.
- Synthesized a new class of amorphous  $\text{Li}_3\text{PS}_4/\text{PEO}$  composite solid electrolytes. Established how thermal annealing affects microstructure and  $\text{Li}^+$  conductivity

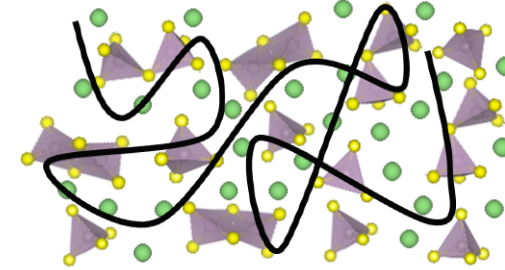


## Summary

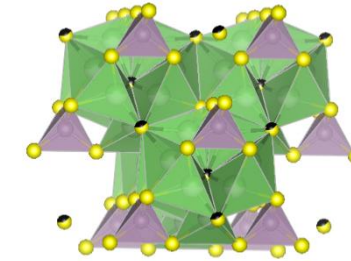
Crystalline  $\beta\text{-Li}_3\text{PS}_4$



Amorphous  $\text{Li}_3\text{PS}_4/\text{PEO}$



$\text{Li}_6\text{PS}_5\text{Cl}$



## Ongoing work:

- Study cathode/electrolyte interfaces in all-solid-state batteries (e.g.,  $\text{Li}/\text{Li}_3\text{PS}_4/\text{LiCoO}_2$ )
- Synthesize argyrodite and halide-doped sulfide SEs with  $\text{Li}^+$  conductivity  $\geq 1 \text{ mS/cm}$  at  $25^\circ\text{C}$
- Develop slurry casting methods to produce SE films  $\leq 30 \mu\text{m}$  thick